

A non-linear equation from photopolymerization kinetics

M. L. Glasser

Department of Physics and Center for Quantum Device Technology
Clarkson University
Potsdam, NY 13699-5820 (USA)

ABSTRACT

In a medium where a photoreactive species produces N equally photoreactive radicals, by combining the Lambert-Beer law for the decay of light intensity, as a beam propagates into the medium, with the kinetic equation, one obtains a generalization of the Wegscheider equation from photobleaching theory. It is shown that this equation can be solved exactly, but implicitly, and can be reduced to a first order ordinary differential equation in a single reduced variable.

Introduction

As a light beam propagates into a medium containing a various photoreactive species the beam intensity decreases with depth due to absorption proportional to the concentration of the active molecules as is described by the Lambert-Beer law [1]. By combining this law with the kinetic equation one obtains a non-linear first order integro-partial differential equation. Situations where the N radicals released lead to desirable effects, such as bleaching and polymerization, have been studied for many years. An extensive list of references is presented in [2]. For the case of a single species the Lambert-Beer law for the light intensity

$$I(x, t) = I_0 \exp[-\alpha \int_0^x C(u, t) du] \quad (1)$$

combined with the kinetic equation

$$\frac{\partial C(x, t)}{\partial t} = -\phi \alpha I(x, t) C(x, t) \quad (2)$$

gives Wegscheider's equation [3]

$$\begin{aligned} \frac{\partial C(x, t)}{\partial t} &= -\phi \alpha I_0 \exp[-\alpha \int_0^x C(u, t) du] C(x, t) \\ C(x, 0) &= C_0. \end{aligned} \quad (3)$$

whose solution has been known for many years [2]. Here C is the concentration, α is the absorption coefficient, and ϕ the quantum yield. For the case of a slab $0 < x < L$, in terms of reduced variables $T = \phi \alpha t$, $z = x/L$, $S_0(z, T) = C(x, t)/C_0$, $\gamma = \alpha C_0 L$, the solution is

$$S_0(z, T) = [1 + e^{-\gamma z} (e^T - 1)]^{-1} \quad (4)$$

which is examined thoroughly in [2].

Systems are presently under investigation [4] where, not only the initial species, whose concentration is C , but its N reaction products all have the same absorption coefficient. A similar analysis leads to the more general equation, expressed in terms of the dimensionless variables given above,

$$\begin{aligned} \frac{\partial C(z, T)}{\partial T} &= -e^{-N\gamma z} \exp[\gamma \int_0^z C(u, T) du] C(z, T) \\ C(z, 0) &= 1. \end{aligned} \quad (5)$$

The aim of this note is to present the exact, albeit implicit, solution to (5).

Calculation

We first introduce the cumulative concentration $\sigma(z, T) = \int_0^z S(u, T) du$ for which $\sigma(z, 0) = z$ and $\sigma(0, T) = 0$. Then by integrating both sides of (5) over z and then differentiating with respect to z , one finds

$$\frac{\partial^2}{\partial z \partial T} [\sigma(z, T) - Nz] = -e^{-\gamma[\sigma(z, T) - Nz]} \frac{\partial}{\partial z} [\sigma(z, T) - Nz]. \quad (6)$$

That is, for $f(z, T) = \sigma(z, T) - Nz$ one has the partial differential equation

$$\frac{\partial^2 f(z, T)}{\partial z \partial T} + \left(\frac{\partial f}{\partial z} + N \right) e^{\gamma f(z, T)} = 0 \quad (7)$$

with $f(z, 0) = -(N-1)z$, $f(0, T) = 0$.

Next, we introduce $V(z, T) = -\log[f_z + N]$ to obtain

$$\frac{\partial^2 V(z, T)}{\partial z \partial T} = -\gamma \frac{\partial}{\partial T} (e^{-V(z, T)} + NV) \quad (8)$$

which, after integration with respect to T becomes

$$\begin{aligned} \frac{\partial V(z, T)}{\partial z} &= \gamma(1 - NV - e^{-V}) \\ V(0, T) &= T. \end{aligned} \quad (9)$$

From (9) we get the implicit relation

$$\int_T^{V(z, T)} \frac{ds}{1 - Ns - e^{-s}} - \gamma z = 0 \quad (10)$$

or, since $S = e^{-V}$, following a simple change of integration variable,

$$\int_{S(z, T)}^{e^{-T}} \frac{du}{u(1 + N \log u - u)} - \gamma z = 0. \quad (11)$$

Finally, in terms of the new variables

$$\begin{aligned} \tau &= \int_{\ln 2}^T \frac{du}{1 - Nu - e^{-u}} \\ \xi &= \gamma z - \tau \\ S(z, T) &= S(\xi), \end{aligned} \quad (12)$$

we find that the solution to (5) has the implicit representation

$$\int_{1/2}^{S(\xi)} \frac{du}{u(1 + N \ln u - u)} = \xi. \quad (13)$$

Discussion

Let us first look at the case $N = 0$, which renders (5) equivalent (under $S = -S_0$) (mathematically, but not physically) to the Wegscheider equation [1]. By explicit integration $\tau = \ln(e^T - 1)$, $S(\xi) = e^\xi(e^\xi + 1)^{-1}$ and we recover the solution (4). Note that (13) is equivalent to the first order ordinary differential equation

$$S'(\xi) = \xi(1 + N \ln \xi - \xi) \quad (14)$$

subject to an appropriate initial condition. Eq. (14) should be useful for obtaining series approximations to $S(z, T)$. It also indicates that for $N > 0$ $S(z, T)$ is nonanalytic along the trajectory $\gamma z = \tau$.

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References

- [1] J.G. Calvert and J.N. Pitts, *Photochemistry*[Wiley, NY (1966)]
- [2] Guillermo Terrones and Arne J. Pearlstein, *Macromolecules* **34**, 3195 (2001).
- [3] R. Wegscheider, *Z. Phys. Chem.***103**, 273 (1923).
- [4] V. Nekkanti (Private communication).